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54 **Process for imaging multi-layer resist structure.**

57 An image is provided by depositing a first layer of a photoresist containing a phenolic-formaldehyde novolak type polymer, and an imidazole, benzimidazole, triazole, or indazoles to increase the solubility of the layer in aqueous alkaline developer after exposure to imaging radiation; depositing on the first layer a second layer of a photoresist containing a phenolic-formaldehyde novolak type polymer; the second layer having a lower degree of solubility in aqueous alkaline developer after exposure to imaging radiation; exposing the layers to imaging radiation; and developing the layers.

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Process for Imaging Multi-Layer Resist Structure

The present invention is concerned with providing an image, and is particularly concerned with providing an image or mask of a multi-layer resist article.

In the manufacture of patterned devices such as semiconductor chips and carriers, the steps of defining different layers which constitute the desired product are among the most critical and crucial steps involved. Polymer films are often used in integrated circuit fabrication as a pattern transfer mask for the semiconductor substrates. For example, polymers used as a photoresist can act as a mask for etching, ion implantation, or lift-off to induce designated removal, doping, or addition to the underlying substrate, respectively.

As the lines and spaces to be etched, however, become smaller, such as at about 1 μm , the photolithographic procedures for producing the photoresist pattern that is the etch mask are affected by such parameters as reflections from the surface grain structure of the metals or polysilicon substrate to be etched, standing wave effects, variations in the photosensitive material thickness, reflections from steps and diffraction effects.

One technique for overcoming the problems of surface topology, reflections and diffractions, is to employ as multi-layer resist system known as a portable conformable mask (PCM) system. Such is described by Burn Jeng Lin, "Portable Conformable Mask - A Hybrid Near U.V. and Deep U.V. Patterning Technique", Proceeding of SPIE, Vol. 174, page 114, 1979, disclosure of which is incorporated herein by reference. The simplest multi-layer resist system employs a two-layer resist system which avoids the cost and complexity of most other multi-layer systems. The bottom layer is insensitive to the radiation used to image the top resist layer, and is preferably a resist from a polymer of methylmethacrylate such as polymethylmethacrylate (PMMA), that is applied over the wafer topology to provide a planar surface. The top layer is generally a relatively thin (e.g., about 1 μm or less) layer of a material that is simultaneously sensitive to the imaging radiation -- electron beam, X-ray, or optical radiation -- and opaque to the radiation used to expose the bottom layer. Typically this can be a positive photosensitive material that responds to the imaging radiation such as ultraviolet light used in step-and-repeat photolithography and is opaque to deep U.V. wavelengths used to expose PMMA. After the top layer is imaged by flood exposure through the top layer resist mask and developed using, for instance deep U.V. (about 190 nm to about 280 nm).

A number of the suggested processes used to overcome image distortion or linewidth variation due to different radiations from the irregular surfaces require processing that is rather complex. This causes a decrease in the throughput and an increase in process control problems.

It has also been suggested to use two layers of the same parent resist of varying molecular weights to achieve different sensitivities or solubilities.

However, such an approach requires unique synthetic effort for control of molecular weight as well as tedious polymer characterizations. It would, therefore, be desirable to provide a method that is capable of overcoming image distortion or linewidth variations due to different radiations from irregular surfaces that does not require the complex processing now employed.

It is the object of the invention to provide a process for forming a multi-layer resist system with said process and its control being simple.

This object is achieved by a process as disclosed in claim 1.

The inventive process achieves the desired profile and overcomes the distortion problems due to different reflective radiations from irregular surfaces without requiring special synthesis or polymer characterizations. Resist patterning pursuant to the present invention requires only one exposure and one developing step to obtain the desired imaged profile.

The modifier is preferably an imidazole, benzimidazole, triazole, or indazole. Mixtures can be employed if desired.

Other advantageous embodiments of the inventive process are disclosed in the subclaims.

The inventive process will become more apparent from the following detailed description.

The first layer of the first resist material employed in accordance with the present invention is a positive resist material.

The positive resist is a phenolic-formaldehyde novolak type polymer sensitized with diazo compounds. Examples of such diazo sensitizers are discussed on pages 48-55 of DeForest, *Photoresist Materials and Processes*, McGraw-Hill Book Company, 1975, disclosure of which is incorporated herein by reference. Some diazo compounds are derivatives of benzoquinone 1. 2-diazide-4-sulphochloride; 2-diazo-1-naphthol-5-sulphonic acid ester; naphthoquinone-1, 2-diazide-5-sulphochloride; naphthoquinone-1, 2-diazide-4-sulphochloride; naphthoquinone 2, 1-diazide-5-sulphochloride. The preferred diazo sensitizers are the diazo-naphthoquinone sensitizers.

The phenolic component of the phenolic novolak polymer includes phenol and substituted phenols such as cresol. A particular example of such is Shipley AZ-1350 which is an cresol-formaldehyde novolak polymer composition. Such a positive resist composition includes therein a diazoketone such as 2-diazo-1-naphthol-sulphonic ester.

The composition usually contains on the order of about 15% by weight or so of the diazoketone compound. Examples of some other commercially available photosensitive materials suitable for providing the first layer of material employed in accordance with the present invention are AZ-1370 and AZ-1470 from Shipley; AZ-4110 and AZ-4210 from AZ Photoresistive Division of American Hoechst; HPR 204 from Phillip A. Hunt; Kodak 820 from Kodak, and OFPR 800 from Tokyo Ohka.

The first layer according to the present invention must also contain an imidazole, triazole, indazoles, tetrazoles, or mixtures thereof. The preferred compounds are the imidazoles with the most preferred being benzimidazole.

Examples of some additional compounds of the above types are imidazole, 1-methyl-imidazole, 1-propyl-imidazole, 2,4-di-methyl-imidazole, 4-methyl-imidazole, 2-isopropyl-imidazole, 2-phenyl-imidazole, 1-benzylimidazole, β -imidazolopropionic acid, 1,2-dimethylimidazole, 1-methyl-2-hydroxymethyl-imidazole, 4-sulfo-imidazole, 2-methyl-4-sulfo-imidazole, 2-(sulphophenyl)-imidazole, 2-isopropyl-4-sulfo-imidazole, 1-n-propyl-5-sulfo-imidazole, 1-n-propyl-4-sulfo-imidazole, 1,2-bis-(1'-imidazolyl)-ethane, 1-(p-sulphophenyl)-imidazole, histidine, 2-(imidazolo-ethyl)-pyridine, 1-(2'-aminoethyl)-imidazole-hydrochloride, 1-(3'-aminopropyl)-imidazole-hydrochloride, 1-methyl-2-carboxymethyl-imidazole, 2-(p-sulphophenyl)-4-sulfo-imidazole, 1-methyl-2-sulfo-imidazole, 2-sulfoimidazole, 1,2-bis-(1'-methyl-5'-imidazolyl)-ethane, 5-sulfo benzimidazole, 5,7-disulfo benzimidazole, tetrazole, indazole, triazole-(1,2,4), 4-ethyl-triazole-(1,2,4), 4-methyl-triazole-(1,2,4), 4-phenyl-triazole-(1,2,4), 3,4,5-trimethyl-triazole-(1,2,4), 4-(p-sulphophenyl)-triazole-(1,2,4), 3-methyl-triazole-(1,2,4), 3-ethyl-triazole-(1,2,4), 3,5-dimethyl-triazole-(1,2,4), 3-phenyl-triazole-(1,2,4), 1-methyl-triazole-(1,2,4), 1-ethyl-triazole-(1,2,4), 1-phenyl-triazole-(1,2,4), 3-sulfo-triazole-(1,2,4), 3-amino-triazole-(1,2,4), 3,5-diamino-triazole-(1,2,4), 1,2-bis-(5'-sulfo-3'-triazolyl)-ethane, 1,2-bis-(5'-amino-3'-triazolyl)-ethane, 1,2-bis-(3'-triazolyl)-ethane, 1,2-bis-(4'-methyl-3'-triazolyl)-ethane, bis-(3-triazolyl)-methane, bis-(5-sulfo-3-triazolyl)-methane, bis-(5-amino-3-triazolyl)-methane, bis-(3-triazolyl)-methane, bis-(5-sulfo-3-triazolyl), bis-(5-amino-3-triazolyl), 3,3'-bis-triazolyl, 1,2-bis-(1'-triazolyl)-ethane, 3-(2'-aminoethyl)-triazole-(1,2,4), β -(1-triazolyl)-propionic

acid, 1,4-bis-(5'-sulfo-3'-triazolyl)-butane, 1,4-bis-(5-amino-3'-triazolyl)-butane, 1-(3-sulfopropyl)-triazole-(1,2,4), 1,2-bis-(4'-triazolyl)-ethane, 1-methyl-triazole-(1,2,3), 1-ethyl-triazole-(1,2,3), 2-ethyl-triazole-(1,2,3), 2-propyl-triazole-(1,2,3), 1-(2'-carboxyethyl)-triazole-(1,2,3), 5-sulfo-benzotriazole, 5,7-disulfo-benzotriazole, benzotriazole, 4-methyl-triazole-(1,2,3), 4,5-dimethyl-triazole-(1,2,3), 4-butyl-triazole-(1,2,3), 4-phenyl-triazole-(1,2,3), 1-(3'-aminopropyl)-triazole-(1,2,3), 1-(2'-aminoethyl)-triazole-(1,2,3), and 1,2-bis-(5'-triazole)-ethane.

These materials are employed in an amount sufficient to increase the solubility of the layer in aqueous alkaline developer after exposure to imaging radiation. These materials are usually present in amounts of about 0.5 % to about 5 % and preferably about 1 % to about 1.5 % by weight of the photoresist.

The first layer is usually about 300 to about 700 nm and preferably about 400 to about 500 nm.

The first layer is commonly referred to as the planarizing layer and generally is thicker than the second layer atop it.

Deposited on said first layer is a second and different positive photoresist layer which differs from the first layer. This second layer contains a phenolic-formaldehyde type polymer and a diazo-sensitizer of the type discussed above for the first layer. The second layer must have a lower degree of solubility than the first layer in aqueous alkaline. The second layer is usually thinner than the first layer and usually about 300 to about 500 nm and preferably about 300 to about 400 nm.

The structure is exposed to imaging radiation and developed. The resist image is typically produced by imaging radiation having a wavelength of about 365 to about 436 nanometers. The exposure is usually from about 60 to about 100 millijoules/cm² and preferably from about 80 to about 90 millijoules/cm².

The exposure to the radiation can be achieved by employing an ultraviolet lamp source.

In addition, if desired, electron beam radiation can be employed as the radiation source. In such a case, the dose of the electron beam imaging radiation is usually at least about 10 microcoulomb/cm² and preferably about 15 microcoulomb/cm².

The exposed portions are removed with an aqueous alkaline solution such as a potassium hydroxide or sodium hydroxide aqueous solution containing about 0.2N % to about 0.28N % of the hydroxide, preferably potassium hydroxide.

The following examples are presented to further illustrate the present invention.

Example 1

Onto a planar silicon substrate is deposited a first layer of about 500 nm of a novolak resist containing about 17-20 % diazonaphthoquinone and about 1.5 % benzimidazole and a second and top layer of about 300 nm of the same novolak resist containing about 17-20 % diazophthoquinone as in the bottom layer, but containing about 0.75 % tetrazole. The structure is exposed to electrons at 25 microcoulombs/cm² at 25 KeV. The exposed films are developed in 0.25 N KOH developer and 0.5 μ m features are resolved with a controlled undercut profile for subsequent lift-off.

Example 2

Example 1 is repeated, except the substrate employed is a silicon substrate with 0.4 μ m silicon dioxide steps. The submicron features are delineated with no evidence of linewidth distortion.

Claims

1. Process for providing an image which comprises:
depositing on a substrate a first layer of a positive photoresist comprising a phenolic-formaldehyde novolak type polymer with a diazo-sensitizer and a modifier in an amount sufficient to increase the solubility of the layer in aqueous alkaline developer after exposure to imaging radiation;
depositing on said first layer a second and different layer of a positive photoresist comprising a phenolic-formaldehyde novolak type polymer with a diazo-sensitizer wherein said second layer has a lower degree of solubility than said first layer in aqueous alkaline developer after exposure to imaging radiation;
exposing said first layer and said second layer to imaging radiation in a predetermined pattern; and
developing said first layer and said second layer.
2. Process according to claim 1, wherein said modifier is a compound selected from the group of imidazoles, benzimidazoles, triazoles, and indazoles, and mixtures thereof.
3. Process according to claim 2, wherein said compound is an imidazole where said imidazole is preferably employed in amounts of about 0.5 % to about 5 % by weight based upon the phenolic-formaldehyde novolak type polymer.
4. Process according to claim 2, wherein said compound is benzimidazole.
5. Process according to any one of claims 1 to 4, wherein said first layer is thicker than said second layer.

6. Process according to any one of claims 1 to 5, wherein said sensitizer is a diazo-naphthoquinone.

7. Process according to any one of claims 1 to 6, wherein said first layer is about 400 to about 700 nm, and said second layer is about 300 to about 500 nm.

8. Process according to any one of claims 1 to 7, wherein said first layer and said second layer are developed with an aqueous alkaline solution with said alkaline solution being preferably a potassium hydroxide or sodium hydroxide aqueous solution where said solution contains most preferred about 0.2N to about 0.28N of the hydroxide.

9. Process according to any one of claims 1 to 8, wherein said imaging radiation has a wavelength of about 365 to about 436 nm with the exposure being preferably from about 60 to about 100 millijoules/cm² and most preferred from about 80 to about 90 millijoules/cm².

10. Process according to any one of claims 1 to 8, wherein electron beam radiation is employed for said imaging radiation with the dose being preferably at least about 10 microcoulombs/cm² and most preferred about 15 microcoulombs/cm².

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EUROPEAN SEARCH REPORT

Application Number

EP 89 10 9194

DOCUMENTS CONSIDERED TO BE RELEVANT																	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)														
Y	EP-A-0 141 389 (BASF AG) * the whole document * - - -	1-10	G 03 F 7/095 G 03 F 7/022														
Y	CHEMICAL ABSTRACTS, vol. 74, Columbus, Ohio, USA B. Broyde: "Exposure of Photoresists. II. Electron and Light Exposure of a Positive Photoresist." page 455; column 1; ref. no. 118349B * abstract * - - -	1-10															
Y	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 26, no. 3b, August 1983, NEW YORK US page 1731 C.T. Horng et al: "New Resist Combination for Forming a Two-Layer Photoresist Lift-Off Mask" - - -	1-10															
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The present search report has been drawn up for all claims																	
Place of search		Date of completion of search	Examiner														
The Hague		11 March 91	HAENISCH U.P.														
<table border="0"><tr><td>CATEGORY OF CITED DOCUMENTS</td><td>E: earlier patent document, but published on, or after the filing date</td></tr><tr><td>X: particularly relevant if taken alone</td><td>D: document cited in the application</td></tr><tr><td>Y: particularly relevant if combined with another document of the same category</td><td>L: document cited for other reasons</td></tr><tr><td>A: technological background</td><td></td></tr><tr><td>O: non-written disclosure</td><td></td></tr><tr><td>P: intermediate document</td><td>&: member of the same patent family, corresponding document</td></tr><tr><td>T: theory or principle underlying the invention</td><td></td></tr></table>				CATEGORY OF CITED DOCUMENTS	E: earlier patent document, but published on, or after the filing date	X: particularly relevant if taken alone	D: document cited in the application	Y: particularly relevant if combined with another document of the same category	L: document cited for other reasons	A: technological background		O: non-written disclosure		P: intermediate document	&: member of the same patent family, corresponding document	T: theory or principle underlying the invention	
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